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MINIMIZING MECHANICAL DAMAGE TO SOFTWOOD CHIPS  
IN PRETREATMENT FOR OXIDATIVE DELIGNIFICATION

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INTRODUCTION

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Chip fiberization, to meet the need to achieve uniform reaction at practical rates in oxidative pulping, is accomplished in a pressurized refiner system with less damage to softwood fibers after longer preheating at higher pressures than used for producing thermomechanical papermaking pulps. Although fiber length was unchanged, evidence was obtained for some mechanical damage to fibers and reduction in breaking length, but stretch increased. Beating and sheet density changes observed in papermaking properties of fibers probably result from their crystalline regions becoming more ordered during chip fiberization — a fundamental point.

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ABSTRACT

Loblolly pine and black spruce chips were fiberized in a pressurized refiner system at about 130 and 160°C after steaming for up to 5.0 min. Scanning electron micrographs showed separation of fibers in the middle lamella region occurred with less disruption of adjacent lamellae at the higher temperature. Fiberized chips were investigated further after delignification by acid chlorite and alkali. Similarly delignified pulps from pin-chips were used as controls. With fiberization at 160°C fiber length distribution was unchanged but zero-span breaking length of handsheets was reduced significantly, and there were easier-to-swell places on the fibers. When fiberization was at about 160°C, delignified pulps, compared with controls, beat more slowly and had relatively lower sheet densities. The likelihood of this resulting from crystalline regions of fibers becoming more ordered is supported by x-ray diffractogram data. Handsheet tests on Valley beaten pulps showed significant reductions on a sheet density basis in tear factor, breaking length, and tensile stiffness as a result of chip fiberization, but stretch increased so that tensile energy absorption was relatively unchanged. Reductions in strength were less for fiberization at the higher temperature.

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# Minimizing mechanical damage to softwood chips in pretreatment for oxidative delignification

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The need for uniform reaction in oxidative pulping and the use of either fiberized chips or thermomechanical pulp to achieve this need has been referred to earlier (1,2). When fiberizing hardwood chips to obtain more uniform reaction the use of a higher steam pressure, corresponding to about 160°C compared with about 130°C resulted in the additional advantage of less fiber damage (1).

This paper, which is an extension of the above work, describes observations on minimizing mechanical damage to fibers, when fiberizing softwood chips in a pressurized refiner system. The results are part of a study on chip pretreatments prior to delignification by chlorine dioxide-alkali or oxygen/alkali.

## RESULTS AND DISCUSSION

### Chip Fiberization

Since minimizing mechanical damage to fibers is facilitated by a trend toward lignin plasticization or softening at elevated temperatures and higher moisture contents, as discussed previously (3), fiberization tests on loblolly pine were carried out as in Table I at elevated temperatures in an Asplund OVP Defibrator using water impregnated chips. The system had a batch-fed chip preheater with a continuously fed refiner. The second half of the chips in the preheater from Runs A and C was used in Runs B and D, respectively.

In Runs A-D, for which the fiberization steam pressure corresponded to about 130°C, when the disc gap was significantly increased there was an increase in the amount of the coarsest material as shown by Bauer-McNett classification data (Table I). However, even for the largest plate gap microscopic examination revealed mechanical damage to fibers as was also observed for hardwood chips fiberized at a

similar temperature (1) and, hence, further fiberization tests on loblolly were carried out at about 160°C in Runs E and F.

One effect of using the higher temperature during chip fiberization is illustrated in Fig. 1. This shows the cleaner separation of fibers with less disruption of lamellae when fiberizing at about 160°C as in Run F compared with fiberizing at about 130°C as in Run D, in spite of the significantly closer plate gap for Run F. The cleaner separation of fibers at the higher fiberization temperature suggests the degree of plasticization of lignin concentrated in the middle lamella region increased significantly between 130 and 160°C. This trend was also observed for hardwoods (1). Examination of fibers from Runs A, B, and C revealed as much or more fiber disruption as shown for Run D.

Black spruce was used for chip fiberization tests in Runs G and H. These runs were similar to Runs C and E except that the time in the preheater was 4 and 4.3 minutes with a feed period of 4 and 1.3 minutes, respectively.

#### Delignification and Evaluation

Since fiberized chips are relatively coarse compared with papermaking pulps, effects of this pretreatment on softwood fibers were considered further after mild chlorite-alkali delignification as in Table II, following which even the coarsest material readily separated into fibers. This facilitated evaluation including comparisons with control fibers from pin-chips, also delignified using sodium chlorite as in Table II. Various modifications of sodium chlorite delignification, including the influence of reaction conditions, are discussed in a recent review (4).

Determination of fiber length distributions revealed that fibers of the chlorite-alkali pulp from Run A were significantly shorter than the corresponding

fibers from pin-chips, as shown in Fig. 2. A similar comparison of pulp from Run D showed much less difference, but the average fiber length was found to be about 5% below the control; Bauer-McNett classification data, reported in Table III, confirmed the indications in Fig. 1 of mechanical damage to fibers when fiberization was at about 130°C.

Comparison of the fiber length distributions for chlorite-alkali pulps from the control and Run E, for which the higher fiberization temperature of about 160°C was used, also revealed significant fiber shortening similar to that observed for Run A. However, increasing the time in the preheater before fiberization from 1.5 to 4.8 minutes in Run F (Table I) resulted in no significant difference between the fiber length histograms for that pulp and the control, as shown in Fig. 2. Note that a preliminary or presteaming time of over 2 minutes and a temperature of about 160°C, based on the use of a 75 psi steam pressure, distinguish these process conditions from those used in commercial thermomechanical pulping plants (6).

Thus, provided sufficient time is allowed for heating the chips, fiber length can be retained when fiberizing at about 160°C. Nevertheless, as shown in Table III, there is significantly more through 100-mesh material in the pulp from Run F than in the control, so there apparently still was some mechanical degradation of the fibers during fiberization even at 160°C.

Further determination of changes in fiber properties as a result of fiberization included Valley beater evaluation and testing of handsheets. This was done for each of the pulps in Table II, the results being given in Table IV.

Plots of data from Table IV generally showed similar trends for the chlorite-alkali pulps when fiberization was at about 130°C (Runs A and G) compared with at

about 160°C (Runs F and H), for both softwoods. For example, for the lower fiberization temperature both pulps had a lower initial freeness and beat more rapidly than the pin-chip pulp controls. Such a faster rate of beating, which reflects easier development of specific surface, is in accord with expectation on the basis of significantly more 100-mesh material (Table III) and more fiber disruption associated with fiberization (Fig. 1). However, for the higher fiberization temperature both pulps unexpectedly beat more slowly than the corresponding controls.

Also of note are the relationships between beating time and sheet density. For the lower fiberization temperature both pulps had higher sheet densities than the controls for similar beating times. Presumably this reflects a significant amount of disruption of the fibers during fiberization at about 130°C as noted in the above comments on rate of beating. However, for the higher fiberization temperature both pulps unexpectedly had sheet densities at similar beating times that were either about equal to (loblolly) or significantly lower than (black spruce) sheet densities for the corresponding controls. A similar trend toward lower sheet densities or less bonded sheets coupled with fiberization of chips at about 160°C was also noted for hardwoods (1). These unexpected relatively lower sheet densities associated with the higher fiberization temperature may result from changes in molecular structure as discussed later on.

The sets of results for both softwoods are similar to those of corresponding controls from pin-chips especially for zero-span breaking length, tear factor, stretch, breaking length, tensile energy absorption and tensile stiffness vs. sheet density. Irrespective of fiberization temperature, both softwoods had a reduction of at least 20% in zero-span breaking length. Thus, even though no reduction in fiber length was detectable in at least one case (Fig. 2), fiberization caused a significant lowering of zero-span breaking length.

Plotted as a function of sheet density, tear factor was higher for both pulps when fiberization was at the higher temperature, but still 5-10% lower than for the corresponding controls. Similar plots for stretch showed that it was about 15% higher than the controls for both softwoods, irrespective of fiberization temperature. However, breaking length was lower for both softwoods as a result of fiberization. Consequently, tensile energy absorption, which reflects both stretch and breaking length, was either near (loblolly) or just below (black spruce) that for the corresponding controls, with detectably better data relating to the higher fiberization temperature. Tensile stiffness was also greater for the higher fiberization temperature, but about 8-12% below the controls. Thus, on a sheet density basis there were significant reductions in tear factor, breaking length and tensile stiffness as a result of fiberization, but stretch increased so that tensile energy absorption was relatively unchanged and some advantages were associated with the higher fiberization temperature of about 160°C.

#### Further Changes During Fiberization

When chip fiberization is at 160°C, in spite of indications of minimized fiber damage such as cleaner separation of fibers (Fig. 1) and no apparent loss in fiber length (Fig. 2), classification data (Table III) as well as pulp beating and handsheet strength data suggest significant changes have occurred in the fibers. The occurrence of some damage to fibers from black spruce chips fiberized at about 160°C (Run H) is revealed in Fig. 3 by the easier-to-swell places on the fibers. Similar places were absent in control fibers obtained from pin-chips and were much more frequent in fibers from fiberization at about 130°C (Run G). Comparable observations were made for loblolly pine.

Since heating causes cellulose to undergo a number of transitions (7) and causes mercerized cellulose to have increased order in the crystalline regions



(8), higher chip fiberization temperature possibly may produce similar changes which would influence beating rate and sheet density as noted above. Results confirming changes in the crystalline regions are presented in Table V. For the pulps in this table the similarities in delignification procedures and yields (Table II), especially for the case of black spruce, make it unlikely that there are any differences in the hemicellulose contents. Hence, the observed decrease in the width of half height of the x-ray diffractogram 002 peak ( $\Delta 2\theta$ ) with heating at about 160°C during chip fiberization indicates the crystalline regions of the fibers have become more ordered. A similar correlation between more order in the crystalline regions of fibers and higher fiberization temperature has been found for red maple. Other work on native celluloses has also shown that exposure to elevated temperatures increases the level of order in the crystalline regions of fibers (9), which further reinforces such an increase is an influence of temperature during fiberization.

It seems possible that causing increased order in the crystalline regions of fibers has been unrecognized as a significant effect of temperature in conventional chemical pulping. In delignification without temperatures causing increased order in the crystalline regions of fibers, comparable papermaking properties may be more difficult to achieve. Thus, it may be advantageous in new processes to include elevated temperatures, as found in this work and also considered by others (10).

#### CONCLUSIONS

When fiberizing chips at about 160°C instead of at about 130°C, separation of fibers occurred with less disruption of lamellae.

At about 160°C, provided sufficient time was allowed for heating the chips, fiber length could be retained.

Nevertheless, there was still some damage to fibers as revealed by a significant reduction in zero-span breaking length and the occurrence of easier-to-swell places on the fibers.

When fiberization was at the higher temperature chlorite-alkali pulps beat more slowly and had relatively lower sheet densities than other pulps.

Handsheet data for chlorite-alkali pulps on a sheet density basis had significant reductions in tear factor, breaking length and tensile stiffness as a result of chip fiberization, but stretch increased so that tensile energy absorption was relatively unchanged.

Fiberization at the higher temperature of about 160°C had the advantage that some reductions in handsheet test data were less.

It is likely that the slower beating and lower sheet densities noted are due to the crystalline regions of fibers becoming more ordered during fiberization.

#### ACKNOWLEDGMENTS

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Table I. Loblolly Pine Chip Fiberization Tests

Chip Impregnation		Run A	Run B	Run C	Run D	Run E	Run F
Initial moisture content, % wet basis		48-51		48-51		48-51	
Final moisture content, % wet basis		65 <sup>a</sup>		68 <sup>a,b</sup>		63 <sup>a</sup>	67 <sup>a</sup>
Asplund OVP Defibrator <sup>c</sup> (batch-fed preheater and continuously fed defibrator)							
Preheating and Fiberization							
Preheater steam pressure, p.s.i./°C			71/158			71/158	78/162
Time to pressure, sec.			45			45	50
Time in preheater before runs, min.			3.0			1.5	4.8
Defibrator steam pressure, p.s.i./°C			28/133			71/158	78/162
Feed period, min.		0-2.5	2.5-5.0	0-2.5	2.5-5.0	0-2.5	0-1.3
Disc gap, 0.001 in.		8	14	16	20	16	12
Bauer-McNett classification, <sup>d</sup> % o.d.f.c.							
On 6 mesh		2.1	17.2	14.2	37.5	25.2	19.3
On 12 mesh		16.7	25.0	27.2	20.2	24.8	22.6
On 35 mesh		51.6	36.5	37.5	25.7	33.3	33.8
On 65 mesh		15.3	8.0	7.3	4.4	6.1	5.3
Through 65 (by difference)		14.3	13.3	13.8	12.2	10.6	19.0

<sup>a</sup>Steamed twice at 15 psi for 2 min, then cold-water impregnated at 78-100 psi for 30-60 min.

<sup>b</sup>Further soaked at 14 psi for 16 hr.

<sup>c</sup>Single disc 20-in. diameter refiner fitted with No. 5821 pattern plates; 100-hp, 1500-rpm motor, peripheral speed 130 ft/sec; feed rate approximately 1 kg o.d. chips per min.

<sup>d</sup>Water temperatures: 21-22°C. Hot-water solubility (TAPPI Standard Method T 207 m-54): A, D and F; 3.1, 3.2, and 3.6%, respectively.

Table II. Preparation of Acid Chlorite-Alkali Pulps

<u>Process Step</u> <sup>a</sup>	<u>Loblolly Pine</u>			<u>Black Spruce</u>		
	<u>Chips</u> <sup>b</sup>	<u>Run A</u> <sup>c</sup>	<u>Run F</u> <sup>c</sup>	<u>Chips</u> <sup>b</sup>	<u>Run G</u> <sup>c</sup>	<u>Run H</u> <sup>c</sup>
Alkali pretreatment						
Sodium hydroxide, % <sup>d</sup>			10			
Temperature, °C			50			
Time at temp, min			60			
Chlorite Oxidation						
Sodium chlorite, %			100			
Acetic acid, %			15			
Temperature, °C <sup>e</sup>	25-40	25-60	25-60	25-50	25-50	25-50
Time, hr	72	25	25	26	12	12
Alkali Reaction						
Sodium hydroxide, %			5			
Temperature, °C			25			
Time, min			60			
Yield, %	65	60	61	65	64	65

<sup>a</sup>Conditions based on procedure of Thompson and Kaustinen (5).

<sup>b</sup>Pin-chips: approximately 3/32x3/32x3/4 inch.

<sup>c</sup>Fiberized chips as in Table I and text.

<sup>d</sup>All materials on o.d. fibrous material basis and all reactions at 8-10% consistency.

<sup>e</sup>Time to reach maximum from ambient about 4 hours.

Table III. Bauer-McNett Classification Data  
for Loblolly Pine Chlorite-Alkali Pulps

	LP-PC(C) <sup>a</sup>	<u>Run</u> A(C)	<u>Run</u> D(C)	<u>Run</u> F(C)
On 12 mesh, %	43.0	29.2	41.0	43.3
On 35 mesh, %	19.0	13.9	13.8	12.6
On 65 mesh, %	33.6	40.2	34.4	32.7
On 100 mesh, %	1.6	2.9	2.0	2.2
Through 100 mesh, % by difference	2.8	13.8	8.8	9.2

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<sup>a</sup>Pulp from loblolly pine pin-chips (Table II).

Table IV. Handsheet Test Data for Acid Chlorite-Alkali Pulps as in Table II

Loblolly Pine Pulps	LP-PC(C) <sup>a</sup>						Run A(C)						Run F(C)					
Beating time, min <sup>b</sup>	7	10	12	14	2	4	8	12	2	4	7	15	2	4	7	15		
Canadian freeness, ml	530	410	340	260	635	560	420	285	695	675	610	340	695	675	610	340		
Density, g/cc	0.55	0.56	0.58	0.58	0.57	0.59	0.61	0.64	0.51	0.52	0.54	0.60	0.51	0.52	0.54	0.60		
Zero-span breaking length, km x yield/65	19	19	18	19	15	15	15	16	13	14	15	15	13	14	15	15		
Elmendorf tear factor x yield/65	131	124	120	115	100	95	83	79	136	130	116	101	136	130	116	101		
Stretch, %	2.0	2.0	2.0	2.1	2.4	2.5	2.4	2.6	2.0	2.2	2.2	2.4	2.0	2.2	2.2	2.4		
Breaking length, km	8.7	9.2	8.9	9.3	7.0	7.7	8.7	9.8	6.4	7.4	7.5	9.0	6.4	7.4	7.5	9.0		
Tensile energy absorption, g cm/cm <sup>2</sup>	67	72	70	78	70	82	86	107	53	67	66	86	53	67	66	86		
Tensile stiffness, Et, kg/cm	600	634	607	614	463	502	554	570	456	486	497	551	456	486	497	551		
Black Spruce Pulps	BS-PC(C) <sup>a</sup>						Run G(C)						Run H(C)					
Beating time, min <sup>b</sup>	2	5	9	13	1	3	8	16	1	8	16	38	1	8	16	38		
Canadian freeness, ml	650	650	580	530	550	505	340	105	690	665	600	335	690	665	600	335		
Density, g/cc	0.64	0.68	0.70	0.71	0.64	0.66	0.69	0.74	0.60	0.64	0.67	0.73	0.60	0.64	0.67	0.73		
Zero-span breaking length, km x yield/65	26	26	25	26	19	19	19	20	17	19	18	19	17	19	18	19		
Elmendorf tear factor x yield/65	82	80	77	76	73	72	68	58	88	78	74	66	88	78	74	66		
Stretch, %	2.3	2.3	2.3	2.2	2.6	2.6	2.5	2.3	2.9	2.6	2.6	2.5	2.9	2.6	2.6	2.5		
Breaking length, km	15.9	15.8	16.3	16.8	11.5	12.3	12.9	13.5	10.1	11.5	12.4	13.3	10.1	11.5	12.4	13.3		
Tensile energy absorption, g cm/cm <sup>2</sup>	130	133	138	134	116	121	127	121	120	117	129	131	120	117	129	131		
Tensile stiffness, Et, kg/cm	739	741	766	785	615	636	660	725	552	632	672	749	552	632	672	749		

<sup>a</sup>LP-PC(C) and BS-PC(C) are loblolly pine and black spruce chlorite-alkali pulps from pin-chips.<sup>b</sup>Valley beater; bedplate load, 4.5 kg.

Table V. Width at Half Height of X-ray Diffractogram 002 Peak

	Chlorite-alkali pulps (Table II)			
	Unheated pin-chips		Fiberized at 160°C	
	Loblolly	Black spruce	Loblolly	Black spruce
	LP-PC(C)	BS-PC(C)	Run F(C)	Run H(C)
$\Delta 2\theta$ , degrees	2.64	2.60	2.12	2.14





A



B

Fig. 1. SEM micrographs showing on-65-mesh fibers from chip fiberization at about 130°C (A; Run D) and 160°C (B; Run F). Note the greater disruption of lamellae in A. 200X.

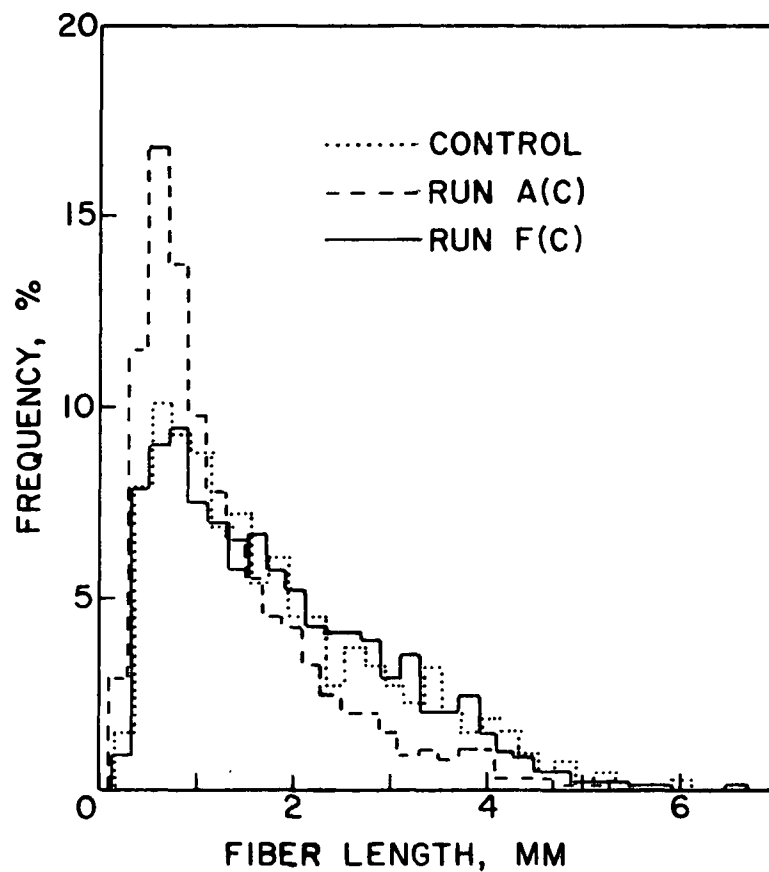
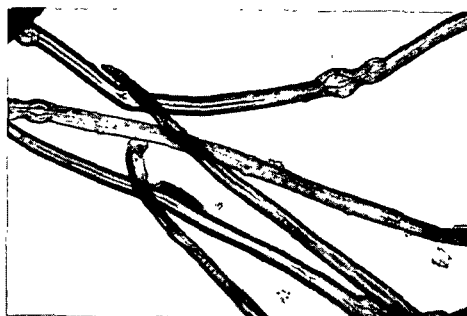
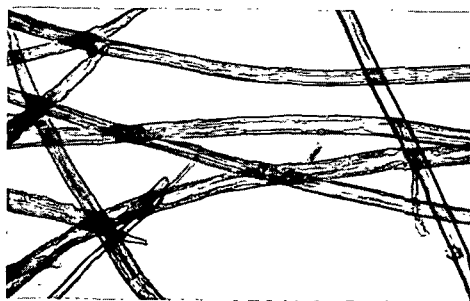


Fig. 2. Comparison of fiber length distributions of loblolly pine chlorite-alkali pulps from chip fiberization at about 130 and 160°C (Runs A and F, Table I) with pulp from pin-chips as control.



A



B

Fig. 3. Chlorite-alkali delignified black spruce fibers treated with cupriethylenediamine solution after staining with Victoria Blue B. With fiberization at about 160°C (A; Run H) there are easier-to-swell places on the fibers which are absent in fibers from pin-chips (B).